Study of the possibilities of polymers surface modification under their treatment in the discharge at atmospheric pressure


MSU, Physical department Vorobjevy gory, Moscow 119899, Russia

Abstract
The present paper represents the method of homogeneous prolonged discharge generation and first results obtained in the field of systematic study of its properties together with results of discharge influence on polymer surface.

1. Introduction

Many techniques are used nowadays for surface modification of polymers resulting in the change of their wetting angle and adhesion improvement. Among them the most prospective and ecologically sate are dry methods: ion beam irradiating of the samples in the presence of the environment gas [1,2], low pressure plasma treatment [3,9] and corona or flame discharge treatment under atmospheric conditions [10-14]. During last years the tendency became evident to develop and utilize discharge at atmospheric pressure more intensively for surface modification of materials due to small cost of the process in comparison with other methods. The review of the literature [14] devoted to this subjects, on the one hand specifies wide opportunities of materials surface modification as a result of processing in the atmospheric discharges, and on the other hand demonstrates absence of detailed understanding of mechanisms of physical processes at atmospheric discharge as well as mechanisms of its influence on a surface under procession. One more problem of the materials treatment under atmospheric conditions is the generation of homogeneous long discharge. The present paper represents the method of homogeneous prolonged discharge generation and first results obtained in the field of systematic study of its properties together with results of discharge influence on polymer surface.

2. Experimental procedure

First experiments of polymer surface modification were carried using pin-plane geometry of the atmospheric discharge, shown on Fig.1. The pin 1 and grounded metal plate2 were separated by the air gap, sample 3 and plastic layer 4. For ignition and sustaining of discharge HF generators 5 with the working frequency 600 kHz and 13.6MHz were used. The additional gas flow was organized with the help of gas distributor 5. The sample, plastic layer and metallic plane were mounted on the coordinate table that gave the opportunity to move the sample relative to the pin in longitudinal and transverse directions. The movement of the
table was controlled by computer. Polymer samples preliminary cleaned by ethyl alcohol were mounted on the plastic layer, then after ignition of the discharge was treated by plasma during multiple scanning of the sample in respect to the needle.

The prolonged discharge was generated with the help of the device schematically shown on Fig.2. The ignition electrode 1 helped to initiate discharge between electrode 1 and metal plate 2. The air flow having longitudinal in respect to the primary discharge and transversal components of velocity on one hand provided necessary properties of the discharge and on the other hand organized the movement of the discharge along the “long” working electrode 3. After reaching the electrode 4 the discharge turns off and the new one is ignited with the help of ignition electrode 1. The increase of transversal gas velocity leads to the increase of the discharge repetition frequency and provides homogeneous treatment of the slowly moving polymer sample with the help of roll drive system.

In order to study discharge properties the volt-ampere characteristics of discharge as well as discharge radiation spectra in dependence on longitudinal and transversal dimensions were measured. Gas temperature was measured on the basis of the rotational structure of the second positive nitrogen band.

3. Experimental results

Experiments with 600kHz and 13.6MHz pin-plate discharges showed that they are quiet different, i.e. discharge at 600kHz has evident filamentary structure while at 13.6MHz without additional gas flow no separate filaments can be seen. In case if pin and plate are separated by large (several cm) gap and discharge is concentrated only near the pin the intensities of nitrogen molecule and ion radiation are maximal near the pin and decrease monotonically with the increase of the distance from the pin, maximum of N2+ radiation being more pronounced. If the distance between pin and plate is reduced and discharge occupies the whole gap between pin and plate one can see the appearance of the second maximum of radiation near the plate (see Fig.3). The presence of dielectric layer between metal plate and discharge does not change qualitatively the observed situation. The appearance of the second radiation maximum can be evidently attributed to the formation of the cathode sheath near the plate as well as near the pin. The presence of the cathode sheath near the plate where the sample under treatment is located manifests that one of the important factors of sample treatment under atmospheric pressure is its irradiation by fast ions accelerated in the sheath similar to that in low pressure plasma. Similar behavior of the discharge radiation one can see in case of prolonged discharge too (see Fig.4). The increase of the gas flow leads to the homogenizing of the nitrogen molecule radiation in the gap between electrodes. The same trend is typical for gas temperature (see Fig.5). The measurements of discharge radiation in transversal direction showed high uniformity of the discharge. It is worth to note that under small gas flowrates the prolonged 13.56MHz discharge exists in homogeneous (not filamentary) mode but the increase of the air flowrate results in the discharge transition to the filamentary one.

The wetting angles of polymers treated under different lengths of atmospheric discharge and different numbers of coherent scanning of the samples in respect to discharge in pin-plane discharge are represented in Fig.6. One can see that treatment of PTFE under atmospheric conditions results in the decrease of wetting angle from 100° to 40°. Ion beam treatment of PTFE in [2] gave the possibility to decrease wetting angle down to 70°. Discharge treatment of vinyl chloride results in reduction of wetting angle down to 40°. It is a bit worse than obtained in [10] but contrary to [10] no ecologically bad gases were used. The reduction of
the contact angle in case of PE was similar to that obtained in [2]. Experiments showed that discharge treatment of the thin polymer film caused its damage due to its overheating. To avoid this effect the length of discharge gap should be significantly increased.

Atmospheric discharge treatment of all considered polymers resulted in significant improvement of their adhesion. The most attention in further experiments was paid to improvement adhesion of PTFE because PTFE has the smallest surface energy and the worst properties from the point of view of adhesion. The results of the study of the adhesion force dependence on the discharge gap length are shown on Fig.7. About 4 times increase of PTFE adhesion was obtained. Polymer treatment in the prolonged discharge gave the opportunity to obtain similar result. Experiments showed that as a result of samples processing in the discharge the wetting angle of the PTFE, PE, PI and vinyl chloride decreased until 40°, 20°, 25° correspondingly, adhesion of PTFE being 4 times stably improved. The change of the wetting angle was stable with respect to the aging effect (see Fig.8).

References


Fig.1. The scheme of pin-plate experiment
1-pin, 2-plate, 3-sample, 4-plastic layer, 5-RF generator.

Fig.2. The scheme of wire-plate experiment
1-ignition electrode, 2-plate, 3,4-working and feeding electrodes, 5-RF generator, 6-sample.
Fig. 3. Dependence of nitogen molecule and molecular ion radiation on distance from pin in case of small (a) and large (b) gas flow rate.
Fig. 4. Dependence of nitrogen molecule and molecular ion radiation on distance from working electrode in case of small (a) and large (b) gas flow rate.

Fig. 5. Dependence of gas temperature on the distance from working electrode. The length of discharge gap is 6 mm.
Fig. 6. Dependence of wetting angle on the discharge gap length in case of pin-plane geometry, 600 kHz.

Fig. 7. Dependence of adhesion on the discharge gap at scanning velocities 100 and 200 mm/s.

Fig. 8. Dynamics of PE wetting angle with time after treatment.